PHOSPHORUS FORMS AND RETENTION

IN SOME SOILS OF LEBANON

By

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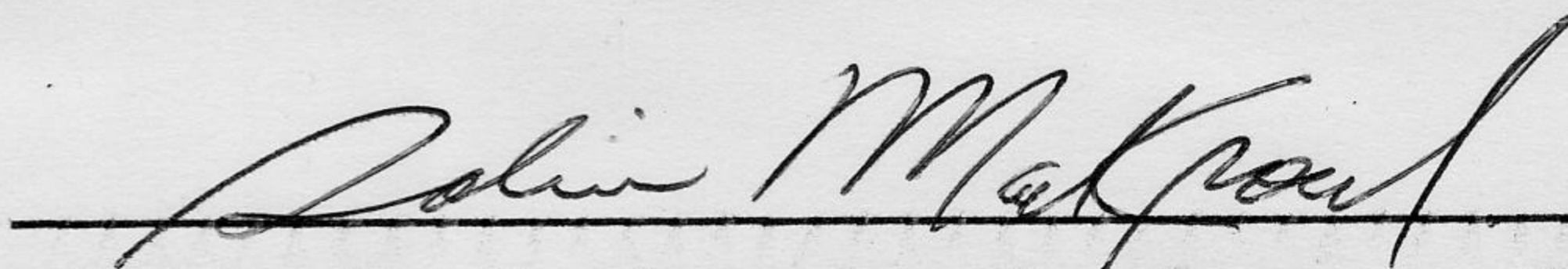MASTER OF SCIENCE IN

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PHOSPHORUS FORMS AND RETENTION
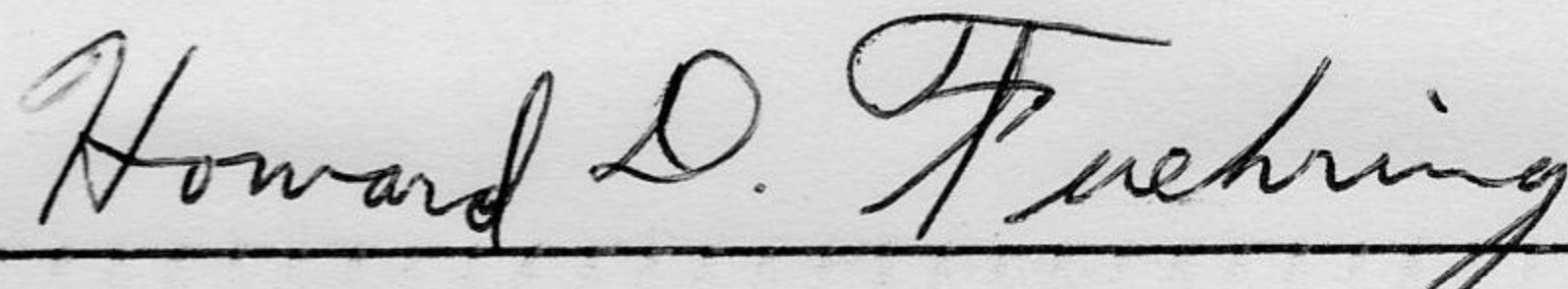# IN SOME SOILS OF LEBANON

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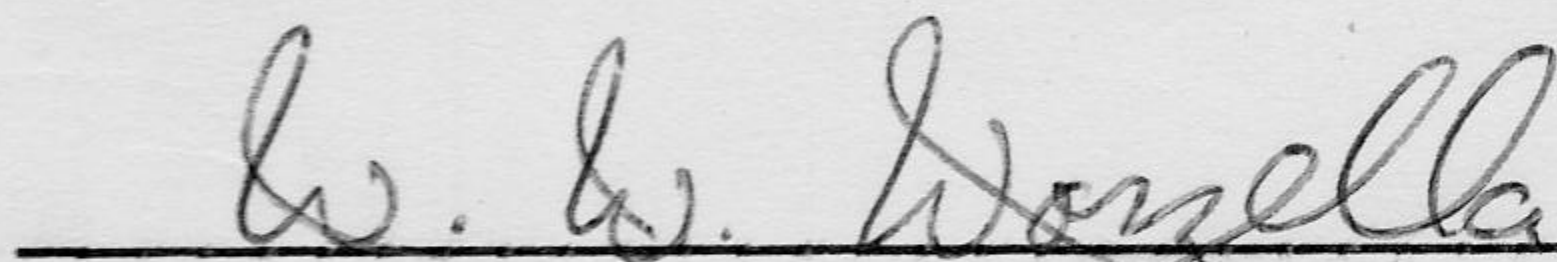ALAUDDIN ABDUL MAJID

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PHOSPHORUS FORMS IN SOILS

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AN ABSTRACT OF THE THESIS OF

Alauddin Abdul Majid for M.S. in Soils.

Title: Phosphorus forms and retention in some soils of Lebanon.

Studies on phosphorus (P) forms and retention in three soil series of Lebanon were conducted in the Division of Soils and Irrigation of the American University of Beirut. The total P was the greatest in the highly calcareous Bazourye series and the least in the slightly calcareous Innsar series. Water soluble and easily replaceable P ranged between 0.2 to 1.6 percent of the total P. In general, the calcareous soils contained more soluble P than the noncalcareous soil. Both Al-P and Fe-P decreased with the $CaCO_3$ content. In spite of the alkaline reaction, Fe-P dominated over Al and Ca-P in the brown noncalcareous Zaoutar series. Ca-P increased with the $CaCO_3$ content and was as high as 88 percent of the total P in the gray highly calcareous Bazourye series. Reductant soluble iron P, occluded aluminum-iron P, and residual P decreased with the increase of $CaCO_3$ content. Organic P increased with the organic matter content and ranged from 6 to 30 percent of the total P. The black Innsar series contained the highest amount of organic P. With the effect of cropping, the forms into which the applied P was changed were in the following decreasing order: Ca-P and water soluble and easily replaceable P in the highly calcareous Bazourye series; Ca-P, Al-P, organic P, and water soluble and easily replaceable P in the slightly calcareous Innsar series; and residual P, Fe-P, Al-P, Ca-P, and organic P in the noncalcareous Zaoutar series.

In general, phosphorus retention in the soils, the clays, and the sand plus silt fractions increased with the time of contact and the concentration of P added. However, the phosphorus retained, when expressed as percent of P added, decreased with concentration. In the soils, phosphorus retention decreased with the increase of $CaCO_3$ and Ca-P contents. It increased with the quantity of Fe-P and Al-P in the soils. Phosphorus retention was the greatest in the noncalcareous Zaoutar series and the least in the highly calcareous Bazourye series. In general, phosphorus retention was higher in

the calcium saturated clays treated for the iron and
aluminum oxide removal than the untreated clays. Phosphorus
retention in the sand plus silt fractions was much less
than that of the clays. The removal of iron and aluminum
oxides from the sand plus silt fractions did not affect
the phosphorus retention in the Innsar series, but it
decreased retention in the Zaoutar series and increased
it in the Bazourye series.

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I. INTRODUCTION

Most of the investigations on phosphorus (P)
behavior in the soils of Lebanon have been done by
indirect methods such as crop response studies and
emperical availability tests (Adams and Sayegh, 1955;
Khan, 1959; Salib, 1961). However, current ideas on this
subject emphasize a fundamental approach to this problem
by chemical characterization of the phosphorus in soils.
In this view, the fractionation of phosphorus is
important. The fractionation of soil phosphorus into the
total amount of each discrete chemical form permits
determination of chemical status of the native phosphorus
and of the fate of the applied phosphate fertilizer with
or without the effect of cropping. The fractionation of
phosphorus is also important because the chemical nature
of each form of soil phosphorus is a factor in determining
its relative effectiveness for crop growth.

The availability of soil phosphorus depends
primarily on its degree of water solubility, since plants
obtain most of their phosphorus from the soil solution
(Olsen and Fried, 1957, p. 97). Therefore, the amount of
added phosphorus that remains available to plants depends
on how much of it remains in readily dissolved forms.

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Among the explanations given for the removal of phosphate ions from the solution when in contact with soils, the most accepted is the retention of phosphate through the process of chemical precipitation and physio-chemical sorption (Hemwall, 1957, p. 95).

The role of the clays and iron and aluminum oxides in the clay fraction in retaining P has been studied by many workers (Toth, 1937; Ghani and Islam, 1946; and others). How much the sand and silt fractions and the iron and aluminum oxides in these fractions are responsible for retaining P has had little reported work.

With these points in mind, a study was conducted to evaluate the different phosphorus forms and the phosphorus retaining characteristics of three soils representing three soil series of South Lebanon.

The objectives of this study were: 1) to fractionate and estimate the amounts of different phosphorus forms; 2) to investigate the phosphorus retaining characteristics of these soils with varying time of equilibration and concentration of P added; 3) to investigate the phosphorus retaining characteristics of the clay fractions with and without the removal of iron and aluminum oxides; and 4) to investigate the phosphorus retaining characteristics of the sand plus silt fractions with and without the removal of iron and aluminum oxides.

II. REVIEW OF LITERATURE

Inorganic Phosphorus Forms in Soils

The development of soil test methods for phosphorus has been mainly concerned with chemical procedures to estimate the easily soluble portion or available P level in soils, considered to have a specific effect in plant nutrition; and the organic and inorganic fractions of soil P as a total which may be correlated to available P. However, it has been emphasized recently that a study of phosphorus fractionation of soils would be a basic approach to the understanding of soil phosphorus behavior.

Kurtz (1953, p. 65) reported that Dean in 1938 in an attempt to fractionate the soil phosphorus, made extractions of soils with NaOH followed by an acid. The alkali extraction was apparently aimed at extracting the iron and aluminum phosphates and the acid extraction was aimed at removing the calcium forms of phosphorus. The portion not removed by these extractants was determined by subtraction from the total P.

Other analytical schemes for the fractionation of soil phosphorus were proposed by Dickman and Bray (1941), Bray and Kurtz (1945), and many other workers. The procedure proposed by Bray and Kurtz (1945) did not aim

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in some of the early methods such as William's (1950a),
was shown to remove not only calcium phosphates but also
a considerable amount of aluminum and iron phosphates.

Aguilera and Jackson (1953) proposed a procedure
for dissolving free iron oxides in soils. They used
sodium dithionite as a reductant and 0.3 $\underline{M}$ Na-citrate as
a chelating agent to dissolve iron oxides in soils.

Bauwin and Tyner (1957a) postulated that the
phosphorus in soils not extracted by acid and alkali
might be occluded in the iron oxide-coatings of weathered
colloidal silicates or in microconcretions (1957b).
Bauwin and Tyner effected the solution of the phosphorus
occluded in free iron oxides by the Deb procedure. They
termed this phosphorus as "reductant soluble" P.

With such criteria, inorganic phosphorus compounds
were classified by Chang and Jackson (1957a) in the
following: water soluble and easily replaceable P
extractable with I $\underline{N}$ NH_4Cl; aluminum bound P (Al-P)
extractable with neutral NH_4F; iron bound P (Fe-P)
extractable with 0.1 $\underline{N}$ NaOH; calcium bound P (Ca-P)
soluble in 0.5 $\underline{N}$ H_2SO_4; reductant soluble iron P
extractable with sodium dithionite and 0.3 M Na-citrate;
occluded iron-aluminum P (barrandite like phosphates
occluded in Fe-oxides) extractable with 0.1 $\underline{N}$ NaOH and
residual P insoluble in all the extractants mentioned
above.

According to Fife (1959a, 1959b), the aluminum-phosphate solubility in systems containing iron hydroxides reaches a minimum value in the vicinity of the neutral point. In view of the almost universal occurrence of free iron oxides in soils it was concluded that satisfactory delineation of Al-P was unlikely to be attained by the use of neutral NH_4F. Fife made use of a fluoride solution apparently sufficiently alkaline to inhibit the resorption of P forms by free iron oxides. Fife (1959a, 1959b) suggested that the most general selective delineation of Al-P in soils would be attained by NH_4F of pH 8.5.

With this background of the development of the analytical techniques for the fractionation of the soil inorganic phosphorus, it is pertinent, for an estimation of soil inorganic phosphorus forms to treat soils successively with: 1) neutral $\underline{N}$ NH_4Cl to extract water soluble and easily replaceable P; 2) 0.5 $\underline{N}$ NH_4F at pH 8.5 to dissolve Al-p; 3) 0.1 $\underline{N}$ NaOH for extracting Fe-P; 4) 0.5 $\underline{N}$ H_2SO_4 for extracting Ca-P; 5) sodiumdithionite and 0.3 $\underline{M}$ Na-citrate to extract reductant soluble iron P and 6) 0.1 $\underline{N}$ NaOH for extracting occluded aluminum-iron P.

Phosphorus Retention

Retained phosphorus is defined for the present study, as the soil phosphorus which has become attached

to the solid phase and which is not water soluble.
"Fixation" was not used in this report to avoid confusion
because the literature is not consistent in the use of
this term. For example, Dean (1949) defined fixed
phosphorus as the soil phosphorus which was not
extractable with water, while the soil phosphorus not
extractable with the dilute acid-fluoride solutions of
Bray and Kurtz (1945) has also been called fixed
phosphorus.

Much of the work in this field has been on acid
soils. Comparatively, there has been little work on
alkaline soils and still less on calcareous soils. The
present study of phosphorus retention was made on alkaline
soils (out of the three soils, two were calcareous) and
this discussion will mainly deal with alkaline and
calcareous soils.

Dean (1949), Olsen (1953), and Hemwall (1957,
p. 104) pointed out that phosphorus retention in alkaline
and calcareous soils was mainly due to the formation of
calcium compounds. However, clay minerals, and iron and
aluminum compounds are also responsible for some retention
of phosphorus in alkaline and calcareous soils.

Role of calcium: The exact nature of calcium compounds
formed in soils is not known. For example, Eisenberger
et al. (1940) reported that there existed a continuous
series of solid solutions between the compounds $CaHPO_4$

and CaO which have an apatite structure. In addition, calcium phosphate can adsorb additional phosphates, thus creating a more complicated system (Eisenberger et al. (1940).

Burd (1948) working with calcareous soils, pointed out that the very general occurrence of potentially soluble compounds in soils and the relatively low solubility of calcium phosphates would lead to the formation of some forms of calcium phosphate upon addition of phosphatic fertilizers. He showed that the concentration of calcium in soil solution was the dominant factor in determining phosphate concentration in the liquid phase of the soil, thus confirming the role of calcium in phosphorus retention.

In addition to the phosphorus retained by the calcium compounds in soils, it also has been suggested that adsorbed calcium on the clay minerals could retain phosphorus. Pratt and Thorne (1948) showed that calcium saturated clays retained far more phosphorus than the clays saturated with sodium. They did not present any information as to whether the calcium phosphate thus formed was precipitated as a distinct phase or was sorbed on the surface of clay particles.

Boischot et al. (1950) in a study of the retention of phosphorus on calcareous sands found that the quantity of P retained was a function of the fineness of the

particles of $CaCO_3$ or directly proportional to the surface area of the particles of calcium carbonate. They explained some of the possible reactions of phosphates with $CaCO_3$. They reasoned that these reactions started with the conversion to a less soluble precipitate of a calcium phosphate with the calcium carbonate furnishing the calcium. The reactions proceeded with excess Ca^{++} and CO_3^{--} being adsorbed onto the surface of calcium phosphate crystals. They showed that the initial phase of reaction was the adsorption of phosphate onto the surface of $CaCO_3$. Therefore, they postulated that the calcium phosphate crystals probably grew on the surface of $CaCO_3$ particles. Boischot et al. further pointed out that, as this adsorption layer increased in thickness, crystal nuclei of a calcium phosphate would form and precipitation would proceed according to the mass action law. The activity of phosphate and calcium remaining in solution after precipitation would depend upon the solubility product constant of the particular calcium phosphate species formed. They reasoned that initially this compound was likely to be dicalcium phosphate, but in the presence of $CaCO_3$ it would slowly change to calcium phosphates richer in calcium, which are less soluble than dicalcium phosphates.

Cole et al. (1953), Olsen and Watanabe (1957), and Cole and Olsen (1959a, 1959b) have done considerable study

on phosphorus adsorption and its solubility in alkaline
and calcareous soils. Their results stress the importance
of surface area of calcium carbonate, clay minerals, etc.
on the adsorption of phosphorus from soluble forms. They
found that these surface phosphates readily equilibrated
with P^{32} and appeared to be closely related to plant
available P. They used the mean activity of $CaHPO_4$ to
express the P solubility and found that P solubility in
calcareous soils was related to the amount of surface area
and the percentage of P saturation of these surfaces.

Role of iron and aluminum compounds: Toth (1937)
demonstrated that the removal of free iron and aluminum
oxides from the clay fraction of soils reduced the
magnitude of phosphorus retention and deduced from this
that these compounds were partially responsible for
phosphorus retention. Many other workers (Kelly and
Midgley, 1943; Perkins and King, 1944; Kurtz et al., 1946;
Ghani and Islam, 1946; Ensminger, 1948; and Swenson et al.
1949, also have postulated and demonstrated that iron
oxides and aluminum oxides play an important role in
phosphorus retention. But only recently has there been a
real effort made to identify the compounds formed and the
mechanisms involved.

Swenson et al. (1949) obtained potentiometric
curves for iron and aluminum chlorides in the presence of
varying amounts of phosphorus. Their curves indicated

that in the pH range of acid soils the compounds formed
were Fe or $Al(H_2O)_3(OH)_2H_2PO_4$ rather than Fe or $AlPO_4$.

Haseman et al. (1950b) studied retention of
phosphorus in relatively pure preparations of individual
clay minerals and hydrous oxides of Fe and Al. All
minerals were characterized by two stages of retention,
one progressing at a rapid rate and another at a much
slower rate. It was concluded that both stages of
retention probably proceeded through similar chemical
reactions of phosphate. The rapid retention resulted
from the reaction of phosphate with readily available Al
and Fe. The slow retention resulted from the reaction of
phosphate with Al and Fe that were released through the
decomposition of respective minerals. Similar findings
were reported by Low and Black (1950).

Kittrick and Jackson (1955a-c) explained phosphorus
retention on the basis of the solubility product principle.
With the help of electron microscope pictures they
observed that a solution-precipitation mechanism was
operative in phosphorus retention (Kittrick and Jackson,
1955a). In the second and third papers (Kittrick and
Jackson, 1955b, c) of this series, they showed that
addition of any iron or aluminum containing minerals to
an equilibrium solution of iron or aluminum phosphate
decreased the concentration of phosphate in the solution
although the solubility product remained essentially

constant.

In the experimental techniques described by Kittrick and Jackson (1955a-c), it was assumed that iron and aluminum compounds formed was precipitated. However, according to Hemwall (1957, p. 99) the results of Kittrick and Jackson do not exclude the possibility that these compounds once formed, also can be adsorbed by the collidal inorganic fractions, like clay minerals, allophane, etc., of soils by Van der Wall's forces. Hemwall's (1957, p. 99) contention is that phosphorus is fixed as a highly insoluble compound with iron and aluminum, which is probably both precipitated and adsorbed under soil conditions. Hsu (1965) explained that precipitation and adsorption of phoshorus resulted from similar chemical forces. He pointed out that whether precipitation or adsorption occurred was dependent on the forms of aluminum and/or iron present at the moment of reaction. Hsu postulated that, in soils, surface reactive amorphous aluminum hydroxides and iron oxides dominated the processes of phosphate retention rather than Al and Fe ions.

Role of the clays and clay minerals: The phosphorus released in the soluble form in soils from weathering of primary phosphorus bearing minerals and additions of plant residues and fertilizer recombines primarily with the clay fraction. As a result the phosphorus of the clay fraction

usually exceeds that of the coarser fractions. Calcium phosphates and aluminum and iron phosphates in the silt and sand fractions usually constitute a very small fraction of the total inorganic phosphorus of soils (Black, 1957, p. 249). For these reasons, the retention study of phosphorus, so far, has been done on the clay fraction and the constituent clay minerals but seldom on silt and sand fractions of soils although there is evidence of presence of hydrated sesquoxides in these fractions (Russel, 1961, p. 75).

The dominating role of crystalline and amorphous iron and aluminum oxides and $CaCO_3$ in fixing P in the clay fraction has already been discussed. In this section, the role of clay minerals as such will be discussed briefly though it is difficult to differentiate between the two, for example, exchangeable Ca can fix phosphorus (Pratt and Thorne, 1948), a phenomenon which may ultimately depend on the cation exchange capacity of clay minerals.

Stout (1939) reported that kaolinite had a large capacity to take up phosphate because of an exchange of phosphate with the layers of hydroxyl ions in the crystal lattice of the mineral. The large capacity of retaining P by kaolinite has been reported by several investigators, Chatterjee and Datta (1951) being among the most recent.

Perkins and King (1944) and Coleman (1942a)

observed little difference between montmorillonite and kaolinite in fixing P. Black (1943) and Coleman (1944a) found that kaolinite retained more phosphate than did montmorillonite at low pH levels but little difference existed above pH 5.0.

Ellis and Truog (1955) hypothesized that aluminum and iron were necessary for clay minerals to retain phosphorus as they reported that montmorillonite would not retain phosphorus once all the free iron and aluminum was removed from the clay.

Mukherjee et al. as cited by Hemwall (1957, p. 100), pointed out that the clay minerals yielded Fe^{+++} and Al^{+++} upon repeated washings with salt solution, a technique used to saturate the cleaned clay fraction with cations.

Low and Black (1950) presented the hypothesis that kaolinite dissociates into aluminum and silicate ions and that phosphate preciphates the aluminum ions, thereby disturbing the equilibrium and causing the clay to dissolve.

In summary, it can be concluded that in alkaline and calcareous soils, the retention of phosphorus is due to the formation of a whole series of insoluble calcium compounds. Further, there is evidence that phosphorus can be retained by the crystalline and amorphous hydrated iron and aluminum oxides in alkaline soils. It can be said that the clay fraction has far more phosphorus retaining capacity than the silt and sand fractions because the

sand and silt fractions have lower content of sesquoxides and far less surface area than the clay fraction.

III. MATERIALS AND METHODS

Soil Sampling[1]

The soil samples for the present study were
obtained from the Government Agricultural Research
Institute, Tell Amara, Lebanon. A fertilizer pot test
was conducted here to evaluate the fertility status of
10 different soils representing 10 soil series of South
Lebanon.

During May, 1964, the samples were collected by the
personnel of the Government Agricultural Research Institute,
Tell Amara. From each location, a bulk sample of
approximately 200 kg was taken to a depth of 30 cm from
6 to 8 points in the field representing about a few dunums
in size. These samples were air dried, the clods crushed
and then sieved through a 5 mm screen to remove larger
stones and gravel . Each sample was thoroughly mixed and
divided into four quarters. A 2 kg sample was used in
each pot.

The experimental design used for the crop response
study was a central composite, rotatable, incomplete

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[1] Information about soil sampling and the fertility
experiment was collected from an unpublished article
of the Govt. Agric. Res. Inst., Tell Amara, Lebanon.

factorial. The variables were the nutrients, N, P, K, S, and Mg. All the nutrients were applied to the soils in solution. The crop grown for the test was wheat.

Wheat was planted in the pots in January, 1965. By the middle of June, 1965, the crop was harvested and the yield data were recorded.

Following the harvest, 2 samples from each of 3 soils were selected and brought from Tell Amara to the Soil Research Laboratory, A.U.B. for the present study of phosphorus forms and its retention. During the crop response study at Tell Amara, one of the two samples of each soil received a high level, and another a low level of P. Identical amounts of N, K, S, and Mg were added to both the samples. The various amounts and sources of fertilizers applied to these soils are given in Table 1.

The three soils used were the black, Innsar series, and the gray, Bazourye series, both from Babliye, and the brown, Zaoutar series from Nabatiye (Anonymous, 1965, pp. 26-33).

The crop roots in the pots were separated from the soils. The soil samples were ground, passed through a 28 mesh sieve, mixed thoroughly, and stored in glass jars. Some physical and chemical characterizations made on these soils are recorded in Table 2.

Table 1. Amounts of various fertilizers
added, mg/2 kg of soil, before
planting wheat. (Tell Amara Study).

Pot receiving low level of P			Pot receiving high level of P		
Source of fertilizer	Nutrient	Amount	Source of fertilizer	Nutrient	Amount
$NH_4(H_2PO_4)$	P	25.0	$Mg(H_2PO_4)_2$	Mg	100.0
	N	11.4		P	254.8
NH_4NO_3	N	24.8	KH_2PO_4	K	100.0
				P	79.4
$MgSO_4$	Mg	75.8	$(NH_4)_2SO_4$	N	87.3
	S	100.0		S	100.0
KNO_3	K	100.0	$NH_4(H_2PO_4)$	N	12.7
	N	35.9		P	28.0
$Mg(NO_3)_2$	Mg	24.2	$Ca(H_2PO_4)_2$	P	37.8
	N	27.9			
Total P		25.0	Total P		400.0

Table 2. Some physical and chemical
characterizations of the soils
used in the study of phosphorus
fractionation and its retention.

Properties	Soil Series				
	Innsar	Zaoutar		Bazourye	
Color (Moist)	10YR 2/1, black	5YR 3/3, dark reddish brown		5Y 6/1, gray	
pH	8.2	7.8		8.3	
C.E.C. (me/100g)	68.0	39.0		25.0	
Organic matter (%)	2.36^x 3.28^{xx}	1.25^x	1.58^{xx}	1.38^x	1.40^{xx}
$CaCO_3$ (%)	3.7	0.0		71.0	
Clay (%)	50.8	46.8		42.8	
Silt (%)	34.2	40.0		41.0	
Sand (%)	15.0	13.2		16.2	
Textural class	Clay	Clay		Silty Clay	

[x] Organic matter in samples receiving the low level of P.
[xx] Organic matter in samples receiving the high level of P.

Analytical Methods

Color: The color of the soils was determined on wet samples from the Munsell soil Color Chart.

Mechanical analysis: The percentage of the sand, silt and clay fractions was determined by the Bouyoucos method (1936), using sodium hexametaphosphate as the dispersing agent. Textural classes were determined by the conventional triangular method.

pH: The pH of the soils was determined in 1:2.5 soil-water suspension using a pH meter with glass electrode.

Organic matter: Organic matter was determined by Walkley-Black method as described by Jackson (1958, pp. 219-221).

Calcium carbonate: The amount of alkaline earth carbonates was estimated by the manometer method of Woodward (1961).

Cation exchange capacity (C.E.C.): The cation exchange capacity of the soil, the clay, and the sand plus silt fractions was determined according to USDA Handbook No. 60.

Organic phosphorus: Organic P was determined by dilute HCl acid extraction after oxidation of organic matter by H_2O_2 (Jackson, 1958, pp. 173-175).

Inorganic phosphorus forms: The inorganic phosphorus fractionation was done according to Chang and Jackson (1957a). They extracted 1 g soil successively with:

1. 50 ml $\underline{N}$ NH_4Cl for estimation of water soluble and easily replaceable P.

2. 50 ml neutral 0.5 $\underline{N}$ NH_4F for dissolving Al-P (two extractions).

3. 50 ml 0.1 $\underline{N}$ NaOH for extracting Fe-P.

4. 50 ml 0.5 $\underline{N}$ H_2SO_4 for Ca-P.

5. 40 ml 0.3 $\underline{M}$ Na-citrate and 3 g of Na-dithionite for extracting reductant soluble iron P.

6. 50 ml 0.1 $\underline{N}$ NaOH for dissolving occluded aluminum-iron-P (barrandite like phosphates occluded in iron oxides).

The procedure of Chang and Jackson (1957a) was exactly followed except for the following modifications.

1. Extraction with NH_4F was done once instead of twice. The pH of NH_4F used was 8.5 instead of 7.0 (Aung Khin and Leeper, 1959).

2. Extraction with H_2SO_4 was done twice, instead of once. According to Aung Khin and Leeper (1959), H_2SO_4 dissolves not only Ca-P, but also a portion of reductant soluble iron P. To correct for this, they suggested that a second extraction should be done which would supposedly dissolve the same amount of reductant soluble iron P as the first extract. The Ca-P was estimated as the P obtained in the 1st H_2SO_4 extraction minus P in the 2nd extract. The total reductant soluble iron phosphate was calculated as the summation of the amounts of this form dissolved in the 1st and the 2nd H_2SO_4 extracts, and P

extracted with Na-dithionite and Na-citrate.

3. Soil samples of the Bazourye series, which contained 71 percent $CaCO_3$, were extracted with 100 ml 0.5 $\underline{N}$ H_2SO_4 instead of 50 ml.

Total P: The total P was determined by the Na_2CO_3 fusion method. The fusion cake was dissolved in dilute H_2SO_4 (Jackson, 1958, pp. 175-176). The P was determined by molybdenum blue method using sulfomolybdic acid solution (Chang and Jackson, 1957a).

Residual P: The P left in the soil sample after the extraction of the various inorganic forms in the process of fractionation was termed residual P. This was determined in the same manner as the total P.

Sample pretreatments and particle size separation: Soil samples were washed with dilute HCl to remove carbonates. Each sample was treated with 30 percent H_2O_2 to destroy organic matter. The H_2O_2 was added slowly while the sample was stirred. The sample was left overnight and then heated on a hot plate and H_2O_2 added slowly until frothing stopped (Jackson 1956, pp. 33-36).

The samples were then transferred to polyethylene centrifuge cups, using distilled water as the flushing and policing liquid. Each sample was washed twice with distilled water. The purpose of the washings was to facilitate subsequent dispersion by removal of the soluble organic matter not completely oxidized by the H_2O_2

treatments, and removal of soluble salts that might be present.

The sample was dispersed in dilute Na_2CO_3 solution (1 g in 9 liters distilled water) with a stirrer. The suspension was centrifuged at 750 rpm for 5 minutes, using a Sorvall Superspeed GSA centrifuge. The centrifugation was done repeatedly until the supernatant liquid was clear. This separated the 2 micron or less clay particles from the sand and silt fractions. The clay and sand-silt fractions were saturated with Ca^{++} by washing 4 times with N $CaCl_2$. To remove the excess salt, the samples were washed twice with distilled water and 3 times with methanol. The samples were dried at 70^oC, ground, and sieved through a 0.5 mm screen. The samples thus prepared were termed "partially clean" clays and "partially clean" sand plus silt fractions.

Separate soil samples, following the removal of $CaCO_3$ and organic matter as described before, were treated with $Na_2S_2O_4$, Na-citrate and $NaHCO_3$ to remove free iron oxides (Jackson, 1956, p. 57). The samples were then boiled in stainless steel beakers with a 2 percent Na_2CO_3 solution. The purpose of boiling with the Na_2CO_3 solution was to destroy amorphous aluminum and silicon oxides which act as cementing agents. The suspension was then transferred to polyethylene centrifuge cups, rinsing with more of the Na_2CO_3 solution. Each sample was centrifuged

at a high speed and the supernatant liquid decanted. The sediments were dispersed with a stirrer in a dilute Na_2CO_3 solution (1 g per 9 liters distilled water). The 2 micron size or less clay particles were separated from the sand plus silt fractions in the same manner as discussed before.

Each fraction was further treated by boiling for 2.5 minutes with 0.5 $\underline{N}$ NaOH to remove allophane, and free Si and Al (Hashimoto and Jackson, 1958). After decanting the liquid, the sediments were transferred to polyethylene centrifuge cups and centrifuged in the supercentrifuge, and washed twice with 1 percent $NaHCO_3$ to remove the NaOH. The supernatant was decanted after each centrifuging. The sediments were then treated for removal of free iron oxides as described previously except for the additional step outlined below. The iron removal treatment was repeated to remove the free iron oxides released by the removal of the amorphous inorganic materials. The additional step was the washing of the sediments twice with a 2:1 acetone-water mixture to remove the citrate ions. The clay and the sand plus silt fractions were saturated with Ca^{++}, washed, dried and ground in the same manner as for the partially clean fractions. The samples thus prepared were called the "clean" clay and the "clean" sand plus silt fractions.

Phosphorus retention study: The phosphorus retention study

was done only on the soil samples receiving the low level of P. The study was made on the three soils and the clean and the partially clean fractions of these soils.

Phosphorus retention by the soils: The retention study was done with varying concentrations of P added. The source of soluble P was KH_2PO_4. To 5 g soil in a 200 ml bottle, 50 ml KH_2PO_4 solution of respective concentrations were added. The concentrations used were 10, 20, and 40 ppm P in solution, which amounted to 100, 200, and 400 ppm P of soils, respectively. The bottles were stoppered, and shaken for 24 hours. Afterwards, they were hand shaken intermittently.

Retention of P from water soluble form was determined at periods of 1, 4, 10, and 30 days. At the appropriate time, 7 ml soil suspensions were taken and centrifuged to separate soils from the liquid phase. Phosphorus in the decanted liquid was determined by molybdenum blue method using sulfomolybdic acid solution (Chang and Jackson, 1957a). The difference between the amount of P added and that remaining in solution was taken as the amount of P retained by the soils.

Phosphorus retention by the partially clean and the clean clays: A similar approach was used to measure the phosphorus retention by the clays as used for the soils. Fifty ml of KH_2PO_4 solution were added to 2 g of clays. The concentrations, 10, 20, and 40 ppm P in solution were

equivalent to 250, 500, and 1000 ppm P of clays. The bottles were shaken in the same manner as for the soils. The determination of P retained by the clays from the water soluble form was done similarly as described previously for the soils.

Phosphorus retention by the partially clean and the clean sand plus silt fractions: The procedure for the determination of P retained by the sand plus silt fractions was similar as used for the soils and the clays except that 40 ml of KH_2PO_4 solution were added to 2 g of sand plus silt fractions. The P added was equivalent to 200, 400, and 800 ppm P of sand-silts.

IV. RESULTS AND DISCUSSION

Phosphorus Forms

Phosphorus characterizations of the three soils studied are given in Table 3. The water soluble and easily replaceable P was higher in the calcareous Bazourye and Innsar series than the noncalcareous Zaoutar series. The soluble form ranged from 0.2 to 1.6 percent of the total phosphorus.

The water soluble and easily replaceable P is readily available to plants. Patel and Mehta (1961) found positive correlation between this form of P and plant uptake of phosphorus. In this view, it appears from the present study that following a high phosphate fertilizer application the calcareous soils are likely to have more available P than noncalcareous soils.

The nature of the water soluble and easily replaceable P is not clearly known. Olsen and Watanabe (1957) explained that this form could be present in varying proportions of calcium, aluminum, and iron bound phosphorus. Since it can be seen that the soluble and easily replaceable P increased with the increase of $CaCO_3$ content (Table 3), most of the water soluble and easily replaceable P in the alkaline soils studies was likely to be associated with calcium. This view is supported by Chang and Chu (1961)

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Table 3. Phosphorus in ppm in the soil receiving low and high levels of P before planting wheat.

Soil series	Levels of P	Soluble[3] P	Al-P	Fe-P	Ca-P	Reductant soluble Fe-P	Occluded Al-Fe-P	Residual P	Organic[4] P	Total P	Total[5] P
Innsar (Black)	L[1]	1.0	20.0	10.0	245.0	10.0	3.8	120.0	173.5	583.3	620.2
	H[2]	12.5	75.0	20.0	320.0	10.0	5.0	117.5	198.5	758.5	840.0
Zaoutar (Brown)	L	2.5	25.0	140.0	35.0	118.8	47.5	257.5	121.3	747.6	820.4
	H	5.0	83.8	205.0	80.0	116.8	48.0	345.0	156.0	1039.6	1110.0
Bazourye (Gray)	L	5.0	31.8	0.0	2162.5	0.0	0.0	90.0	146.0	2435.3	2535.3
	H	42.5	40.0	0.0	2285.0	0.0	0.0	100.0	150.0	2617.5	2705.2

1 Samples receiving 25 mg P per 2 kg of soils.

2 Samples receiving 400 mg P per 2 kg of soils.

3 Water soluble and easily replaceable P.

4 Organic P determined on separate samples.

5 Total phosphorus determined on separate samples.

Table 3. Phosphorus in ppm in the soil receiving low and high levels of P before planting wheat.

Soil series	Levels of P	Soluble[3] P	Al-P	Fe-P	Ca-P	Re-ductant soluble Fe-P	Occluded Al-Fe-P	Re-sidual P	Or-ganic[4] P	Total P	Total[5] P
Innsar (Black)	L[1]	1.0	20.0	10.0	245.0	10.0	3.8	120.0	173.5	583.3	620.2
	H[2]	12.5	75.0	20.0	320.0	10.0	5.0	117.5	198.5	758.5	840.0
Zaoutar (Brown)	L	2.5	25.0	140.0	35.0	118.8	47.5	257.5	121.3	747.6	820.4
	H	5.0	83.8	205.0	80.0	116.8	48.0	345.0	156.0	1039.6	1110.0
Bazourye (Gray)	L	5.0	31.8	0.0	2162.5	0.0	0.0	90.0	146.0	2435.3	2535.3
	H	42.5	40.0	0.0	2285.0	0.0	0.0	100.0	150.0	2617.5	2705.2

1 Samples receiving 25 mg P per 2 kg of soils.
2 Samples receiving 400 mg P per 2 kg of soils.
3 Water soluble and easily replaceable P.
4 Organic P determined on separate samples.
5 Total phosphorus determined on separate samples.

who reported that the kind of phosphorus compounds formed would be dependent on the solid phases on which the phosphates are adsorbed.

In the crop response experiment with wheat on these soils, the water soluble and easily replaceable P, especially in the samples receiving the high level of P reflected well in the grain plus straw yields of wheat (Appendix Table 9).

In the samples receiving the low level of P, Al-P was higher in the highly calcareous Bazourye series than the other two soils which contained about the same amount of this form (Table 3). However, in percent of the total P, Al-P was the least in the Bazourye series (Table 4). In the samples receiving the high level of P, Al-P decreased with the $CaCO_3$ content (Table 3). When calculated as percent of the total P, the Al-P in the Innsar and Zaoutar series increased in the samples receiving the high level over the samples receiving the low level of P.

The Fe-P was the greatest in the noncalcareous Zaoutar series. The highly calcareous Bazourye series contained only a trace amount of this form. From the brown color of the Zaoutar series it appears that the comparatively high Fe-P content is due to the presence of a high amount of iron oxides.

In general, both Al-P and Fe-P decreased with $CaCO_3$ content. The results are in agreement with the

Table 4. Amounts of phosphorus forms expressed as percent of total phosphorus in the soils receiving low and high[2] levels of P before planting wheat.

Soil Series	Levels of P	Soluble[3] P	Al-P	Fe-P	Ca-P	Reductant soluble Fe-P	Occluded Al-Fe-P	Residual P	Organic P
Innsar (Black)	L[1]	0.2	3.4	1.7	42.0	1.7	0.6	20.6	29.8
	H[2]	1.6	9.9	2.6	42.2	1.3	0.7	15.5	26.2
Zaoutar (Brown)	L	0.3	3.3	18.7	4.7	15.9	6.4	34.5	16.2
	H	0.5	8.1	19.7	7.7	11.2	4.6	33.2	15.0
Bazourye (Gray)	L	0.2	1.3	0.0	88.8	0.0	0.0	3.7	6.0
	H	1.6	1.5	0.0	87.4	0.0	0.0	3.8	5.7

1 Samples receiving 25 mg P per 2 kg of soils. 3 Water soluble and easily replaceable P.
2 Samples receiving 400 mg P per 2 kg of soils.

corresponding data of Sen Gupta and Cornfield (1962).

It is generally believed that Fe and Al-P predominate in acid soils and as the pH increases the quantity of these forms decreases (Chang and Jackson, 1958). In the present study the pH of the soils ranged between 7.8 to 8.3, still all the soils contained more than 20 ppm P as Al-P. In percent of the total, this form was very low in the highly calcareous Bazourye series. But in the slightly calcareous Innsar and the non-calcareous Zaoutar series about 8 percent of the total phosphorus occurred as Al-P. Iron bound phosphorus (Fe-P) was not dominant in the calcareous soils, but in the non-calcareous Zaoutar series, Fe-P dominated over the other forms except residual P (Table 4).

Existence of high quantities of Al-P and Fe-P were also found by Patel and Mehta (1961) in some alkaline and calcareous soils of India. They explained this behavior by presuming that in a soil containing an appreciable quantity of iron and aluminum, a considerable quantity of phosphorus must have gone into combination with iron and aluminum during the ages of weathering. However, the increase of the amount of Fe-P and Al-P in the samples receiving the high level over those receiving the low level of P (Table 3) cannot be explained by weathering processes because this increase happened over a period of one year only. The explanation stated below was given by

Hsu and Jackson (1960) for the presence of Al-P and Fe-P
in alkaline soils and seems to be more possible for the
soils investigated in the present study. They attributed
this phenomenon to the local acidity in root and leaching
channels where the effect of bases like Ca is not dominant.

Regarding the availability of Fe and Al-P to plants,
it is believed that the degree of crystallinity, age and
proportion of metal, hydroxide, and phosphate ions are the
main characteristics that determine the availability of
Al-P and Fe-P. In the present study only the amounts of
aluminum and iron bound phosphorus were estimated
irrespective of their properties such as crystallinity,
surface area, etc. Patel and Mehta (1961) found low
positive correlation between the iron and aluminum
phosphates and plant available phosphorus. From this
discussion, it can be said that since the total quantity of
Fe and Al-P was more in the Zaoutar series, plants in this
soil would tap more phosphorus from the source of Fe and
Al-P than the plants in the other two soils. That the Fe
and Al-P are not comparatively a good source of available
phosphorus is also reflected in the yield of wheat grain
plus straw (Appendix Table 9). The Zaoutar series yielded
least.

Phosphorus in the form of Ca-P was in considerably
greater amount in the highly calcareous Bazourye series
than in the other two soils (Table 3). When calculated as

the percent of the total P, the highly calcareous Bazourye series contained about 90 percent of the total phosphorus as Ca-P. The proportion of Ca-P was the least in the noncalcareous Zaoutar series. The Ca-P increased with the $CaCO_3$ content. Similar results were obtained by Sen Gupta and Cornfield (1962).

The yield of wheat grain plus straw (Appendix Table 9) was higher in the soils dominated by Ca-P than in the soil in which Fe and Al-P were dominant. Ca-P in the soils studied is possibly more available to plants than Fe and Al-P. However, though the calcareous soils possibly contained a greater amount of available P with the low phosphate application as evident from the yield data, the response to applied P was higher in these soils than in the noncalcareous soil. Moreover, the A-values of the soils (Appendix Table 10) studied were not consistent with the yields of wheat grain plus straw. Therefore, further studies are needed to evaluate the different phosphorus forms in these soils as to their availability to plants.

Reductant soluble iron P and occluded aluminum-iron P both of which are occluded in iron oxides decreased in order: Zaoutar, Innsar and Bazourye series.

The mechanism of the formation of occluded aluminun and iron P was given by Hsu and Jackson (1960). They explained that during ages of weathering, occlusion of

iron and aluminum phosphates occurs through the process of formation of iron oxide coating on the particle surfaces during the dissolution of iron phosphate, which prevent further dissolution of the rest of iron and aluminum phosphate particles. The difference between the reductant soluble iron P and occluded aluminum-iron P is that the former is simply Fe-bound phosphorus the latter is barrandite like-iron and aluminum together reacting with phosphates. Chang and Jackson (1958) explained that the occluded forms of iron and aluminum P must be through a slow process and not much affected by the recent fertilizer application. In the present study also it was found that the difference in the levels of P did not make any difference in the amounts of these forms.

Occluded iron and aluminum phosphates probably are not available for plant use, except through the unusual degree of poor drainage (paddy fields) under which condition iron oxides reduction may be effected (Chang and Jackson, 1958). For this reason, it can be said that these forms probably do not contribute toward P for plant use in the soils investigated in the present study.

The phosphorus which could not be extracted by the acid, alkali and $Na_2S_2O_4$-citrate was termed residual P. The residual P followed the same trend as the occluded P forms. It was the greatest in the noncalcareous Zaoutar series and the lowest in the highly calcareous Bazourye

series (Table 3). The proportion of this form varied from 4 to 34 percent of the total P (Table 3).

The value of the residual phosphorus is not clearly known and has not been studied extensively. Dean in 1938 as cited by Kurtz (1953, p. 66), found this residual phosphorus to be unaffected by cropping showing that this fraction was not important for crop production.

The organic P ranged between 6 to 30 percent of the total P. It was the highest in the Innsar series. The organic phosphorus seems to be directly related to the organic matter content in the soils studied (Table 2). Similar results were found by Thompson and Black (1950), Williams (1950b), and Thompson et al. (1954). They explained that the direct relation of the organic P with the organic matter of mineral soils was for the reason that organic matter contains carbon, nitrogen, and phosphorus in a roughly constant ratio. The difference between the organic P in the samples of a soil receiving the two levels of P might be due to higher amount of root-lets left in the pots receiving the high level of P because of higher yield in these pots.

The work of Williams (1950c) indicates that organic P is of less importance than inorganic P for plant use. Eid et al. (1953) postulated that organic P by itself is of little value in the phosphorus nutrition of plants. They observed that it becomes of value when it is

mineralized to inorganic forms.

The difference between the added total and the total P determined on separate samples was not much (Table 3). It ranged from 3 to 11 percent of the added total.

The fate of applied phosphorus: To investigate the fate of applied P in the soils under study, Table 5 was made. The figures in this table represent the difference in the amounts of phosphorus forms between the samples receiving the low and the high level of P expressed as percent of the difference between the total P of the two levels.

The applied phosphorus in the calcareous Bazourye series existed mainly as Ca-P and water soluble and easily replaceable P. The comparatively high value of the soluble and easily replaceable P might be due to high degree of phosphorus saturation as evident from the relatively large quantity of total P of this soil (Table 3). Another reason might be that phosphorus in calcareous soils is comparatively loosely bound (Russel, 1961, p. 486). In the Innsar series which was slightly calcareous the applied P combined mainly in the forms of Ca-P and Al-P followed by organic P and soluble P (Table 5). In contrast to the calcareous soils, the applied P in the noncalcareous Zaoutar series was distributed in a variety of forms and decreased in order: residual-P, Fe-P, Al-P, Ca-P, and organic-P (Table 5).

Table 5. Differences in the amounts of P between the samples receiving low[1] and high[2] levels of P, expressed as percent of the difference between the total P of the two levels.

Soil series	Soluble[3] P	Al-P	Fe-P	Ca-P	Reductant soluble Fe-P	Occluded Al-Fe-P	Residual P	Organic P
Innsar (Black)	6.5	31.4	5.7	42.8	0.0	0.7	-1.4	14.3
Zaoutar (Brown)	0.9	20.1	22.3	15.4	-0.7	0.2	29.9	11.9
Bazourye (Gray)	20.6	4.5	0.0	67.2	0.0	0.0	5.5	2.2

1 Samples receiving 25 mg P per 2 kg of soils.
2 Samples receiving 400 mg P per 2 kg of soils.
3 Water soluble and easily replaceable P.

Chang and Chu (1961) explained that the first step in the reaction of soluble phosphate with the various cations occurs on the surface of solid phases with which the phosphate comes in contact. The specific surface areas of the solid phases associated with aluminum, iron and calcium ions determine the relative amount and kinds of phosphates formed. They explained that in course of time phosphorus forms would be changed to iron phosphate depending on the activities of iron and other cations. In the present study, the dominance of Ca-P in calcareous soils might be due to high surface area associated with $CaCO_3$. In the noncalcareous Zaoutar series, in absence of $CaCO_3$, the Ca-P changed to Al-P and mainly Fe-P. It might be due to existence of comparatively high quantity of iron oxides in this soil.

In summary, the phosphorus fractionation study of the soils indicated that soluble phosphorus added to the soils would result mainly in the active forms of Ca-P and the water soluble and easily replaceable P in the highly calcareous Bazourye series; Ca-P, Al-P, and the soluble P in the slightly calcareous Innsar series; and in the active forms of Fe-P, Ca-P, and Al-P in the noncalcareous Zaoutar series. Conversion of applied P to unavailable forms was greater as the proportion of $CaCO_3$ in the soils decreased.

Phosphorus Retention

Phosphorus retention by the soils: Phosphorus retention
study was conducted on three soil series with varying
concentration of P at different periods of time.

In the soils, phosphorus retention increased with
the time of contact and the concentration of P added
(Table 6). The P retained as percent of P added decreased
with the increase of concentration. Similar results were
found by Hibbard (1935) and Low and Black (1950). In
general, the rate of phosphorus retention slowed down
starting on the 10th day of retention.

Phosphorus retention was the highest in the Zaoutar
series. Retention by the end of the first day was as high
as 94, 95, and 87 percent of the added 100, 200, and 400
ppm P, respectively. In contrast, the retention in the
first day varied from 84 to 63 percent in the Innsar
series and 73 to 42 percent in the Bazourye series. The
retention values in the Zaoutar series is thought to be
due to higher iron and aluminum oxides content which
helped the formation of more Fe-P and Al-P in this soil
(Table 4, p.30). There was not much decrease in the per-
cent of P added as the concentration was increased,
probably, because of the presence of the iron and aluminum
oxides in this soil. The retention was more instantaneous
in the noncalcareous Zaoutar series than the other two

Table 6. Phosphorus retention by the soils at varying time and concentrations of P added.

Soil Series	Clay (%)	P added, ppm of soil	Time of fixation							
			1 day		4 days		10 days		30 days	
			ppm[1]	%[2]	ppm	%	ppm	%	ppm	%
Innsar (Black)	50.8	100	84	84	88	88	89	89	93	93
		200	148	74	153	76	164	82	180	90
		400	251	63	261	65	293	73	305	76
Zaoutar (Brown)	46.8	100	94	94	96	96	97	97	99	99
		200	190	95	191	95	195	97	198	99
		400	349	87	364	91	378	94	386	96
Bazourye (Gray)	42.7	100	73	73	83	83	88	88	92	92
		200	138	69	145	72	161	80	175	87
		400	168	42	236	59	281	70	296	74

1 P retained, ppm of soils.
2 P retained, percent of P added.

calcareous soils probably because the iron and aluminum oxides precipitated the phosphate ions within a short period of time (Kittrick and Jackson, 1955a). This explains why it took for the two calcareous soils as long as 30 days to retain the same amount of P as was retained by the non-calcareous Zaoutar series on the first day. The slow retention in the calcareous soils might be due to the initial surface reaction of phosphate ions with $CaCO_3$ and to the slow precipitation of calcium phosphates in course of time (Boischot et al., 1950).

The phosphorus retention on the first day was higher in the slightly calcareous Innsar series than the highly calcareous Bazourye series (Table 6). The higher retention in the Innsar series might be due to the presence of higher amount of iron and aluminum oxides and to the lower $CaCO_3$ content in this soil compared to the Bazourye series. However, in course of time, the amounts of phosphorus retained were almost equal in the two calcareous soils probably because of association of P with $CaCO_3$ as explained previously (Boischot et al., 1950).

The Bazourye series retained the least amount of phosphorus (Table 6). This was probably due to high Ca-P and a trace of Fe-P formation in this highly calcareous soil as evident from the phosphorus fractionation study (Table 4, p. 30). This is supported by Olsen and Watanabe (1957) who explained that in calcareous soils phosphorus

retention is low because of association of P with $CaCO_3$. The low retention in the Bazourye series might also be due to the comparatively high saturation of this soil with phosphorus. This is evident from the high amount of the total phosphorus in this soil (Table 3, p. 28).

Phosphorus retention by the clays: The phosphorus retention study was done with the partially clean and the clean clay fractions. The clean fraction was treated for the removal of iron and aluminum oxides while these compounds were not removed from the partially clean fraction. However, both fractions were treated for the removal of organic matter and carbonates. The purpose of this was to investigate the influence of free iron and aluminum oxides on the phosphorus retention in the clays of the alkaline soils. In addition, the effect of time of reaction and concentration of phosphorus added was also studied. All the clays were Ca-saturated.

In the Innsar and the Bazourye series, the clean clays retained more phosphorus than the partially clean clays. This showed that the removal of iron and aluminum oxides did not decrease but rather increased the retention of P. This finding is not unusual. Similar results were obtained by Ellis and Truog (1955) who studied phosphorus retention in Ca-saturated montmorillonite clays. The clays of the Innsar and the Bazourye series seem to belong to the smectite group as evident from the high cation exchange

capacities (Table 7). According to Ellis and Truog, the slight increase in the cation exchange capacity due to the removal of iron and aluminum oxides did not appear to be an adequate explanation for the large increase in the phosphorus retention. They postulated that since the retention in the Ca-saturated samples appears to be a surface reaction, the only logical explanation for the increased retention would appear to be that the removal of iron and aluminum oxides dispersed the clay thus resulting in more effective surface area for the retention reaction. Another plausible explanation, according to them, would be that the amount of calcium dissociated from the clay was increased in the clean clay thus resulting in more phosphorus retention as calcium bound phosphorus.

In the Innsar series, the clean clay retained most of the phosphorus in the first day from all the concentrations, while it took 10 days to retain as much by the partially clean clay from only the 250 ppm P. The partially clean clay retained about 84 and 60 percent of the added 500 and 1000 ppm P, respectively, over a period of 30 days. This shows that the retaining surfaces of the partially clean clay were comparatively saturated.

Phosphorus retention in the clays of the Bazourye series both with and without the removal of iron and aluminum oxides was lower than in the clays of the Innsar

Table 7. Phosphorus retention by the partially clean and the clean clays at varying time and concentrations of P added.

Soil series	Fraction	C.E.C. me/100 g	P added, ppm of clays	Time of retention							
				1 day		4 days		10 days		30 days	
				ppm[1]	%[2]	ppm	%	ppm	%	ppm	%
Innsar (Black)	Partially clean clay	83.7	250	174	67	206	82	234	94	240	96
			500	259	52	340	68	396	79	420	84
			1000	425	42	443	44	578	58	586	59
	Clean clay	84.8	250	232	93	240	96	244	98	246	98
			500	480	96	487	97	487	97	492	98
			1000	940	94	962	96	974	97	980	98
Zaoutar (Brown)	Partially clean clay	43.5	250	232	93	232	93	236	94	244	98
			500	441	88	447	89	466	93	475	95
			1000	783	78	802	80	828	83	835	83
	Clean clay	44.6	250	215	86	220	88	240	96	248	99
			500	408	82	410	82	466	93	476	95
			1000	775	77	790	79	940	94	960	96
Bazourye (Gray)	Partially clean clay	50.5	250	5	2	18	7	19	8	98	39
			500	51	10	65	13	100	20	170	34
			1000	325	32	560	56	571	57	576	58
	Clean clay	51.7	250	175	70	196	78	218	87	232	93
			500	358	72	375	75	425	85	435	87
			1000	725	72	742	74	825	82	840	84

[1] P retained, ppm of clays.　　　[2] P retained, percent of P added.

series. The lower retention in the Bazourye series might be due to the lower cation exchange capacity in these clays than the clays of the Innsar series. The phosphorus associated with Fe and Al was very low in the highly calcareous Bazourye series. So it was possible that the clay properties were the main factors determining phosphorus retaining characteristics of the clays of this soil.

Unlike the other clays, the phosphorus retention in percent of P added in the partially clean clay of the Bazourye series increased with concentration. This unusual phenomenon could not be explained. Further studies may help in explaining this observation.

In contrast to the two calcareous soils, the phosphorus retention in the noncalcareous Zaoutar series, from all the concentrations up to the 4th day, was slightly higher in the partially clean than the clean clay. The higher retention by the partially clean clay is attributed to the presence of iron and aluminum oxides. In 30 days there was not much difference in retention between the partially clean and the clean clay with the concentrations of 250 and 500 ppm P. But with the concentration of 1000 ppm P, the phosphorus retention by the clean clay exceeded that by the partially clean clay after the 4th day. This might be, as explained previously, due to the greater surface area in the clean clay and

adsorption of calcium bound phosphorus on these surfaces.
The adsorption of calcium bound phosphorus was not so
pronounced in the beginning, probably, because of the
quick precipitation of phosphate by the high amount of
iron and aluminum oxides in the partially clean clay.
Phosphorus retention by the sand plus silt fractions:
Phosphorus retention was studied in the partially clean
and the clean sand plus silt fractions in the same manner
as for the clays. In all the series, phosphorus retention
by the sand plus silt fractions both with and without the
removal of iron and aluminum oxides, increased with the
time of contact and the concentration of P added (Table 8).

In the Innsar series, the phosphorus retention by
the partially clean sand plus silt fractions was almost
equal to that by the clean fractions (Table 8). This
might be due to the low content of iron and aluminum
oxides in this soil, the removal of which did not make any
difference in phosphorus retention.

Phosphorus retention in the Zaoutar series was
higher in the sand plus silt fractions not treated for the
removal of iron and aluminum oxides than the treated
fractions. The effect of iron and aluminum oxides was
more pronounced in the Zaoutar series because this soil
contained more P associated with Fe and Al than in the
other two soils.

The sand plus silt fractions showed a different

Table 8. Phosphorus retention in ppm by the partially clean and the clean sand plus silt fractions at varying time and concentrations of P added.

Soil series	Fraction	C.E.C. me/100 g	P added, ppm of sand-silt	Time of retention			
				1 day	4 days	10 days	30 days
Innsar (Black)	Partially clean sand-silt	5.3	200	7	20	31	43
			400	52	70	82	100
			800	107	120	128	133
	Clean sand-silt	3.9	200	9	19	30	41
			400	51	63	76	91
			800	105	106	118	120
Zaoutar (Brown)	Partially clean sand-silt	3.2	200	25	63	69	71
			400	37	65	89	92
			800	45	69	91	96
	Clean sand-silt	2.9	200	5	20	31	35
			400	33	44	50	53
			800	35	55	56	60
Bazourye (Gray)	Partially clean sand-silt	3.0	200	14	14	15	16
			400	30	31	31	32
			800	38	40	40	41
	Clean sand-silt	2.7	200	52	84	132	134
			400	60	116	300	301
			800	74	138	300	302

pattern of retention in the Bazourye series. Phosphorus retention was higher in the sand plus silt fractions with the iron and aluminum oxides removal treatment than the fractions without the treatment. A similar trend in retention was found in the clays of this soil. The higher retention in the clean than the partially clean clay was explained by presuming that the effective surface area increased in the clean clay due to the dispersion of the clays by the removal of iron and aluminum oxides. But the similar phenomenon is very unlikely in the sand plus silt fractions because of small surface area of these fractions. The higher retention in the clean sand plus silt fractions might be due to some changes in chemical properties of the minerals of the sand and silt during the process of cleaning. A little amount of sesquoxides might have been formed due to the possible decomposition of feldspars etc., of the sand plus silt fractions.

V. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Studies on phosphorus forms and its retention in three soil series of Lebanon were conducted in the Division of Soils and Irrigation of the American University of Beirut. The objectives of these studies were to fractionate and estimate the different forms of soil phosphorus; to investigate the phosphorus retaining characteristics of these soils; and to investigate the role of iron and aluminum oxides in retaining phosphorus in the clay and the sand plus silt fractions of these soils.

In the fractionation study, inorganic phosphorus was classified into: water soluble and easily replaceable P extracted with $\underline{N}$ NH_4Cl; Al-P extracted with 0.5 $\underline{N}$ NH_4F; Fe-P extracted with 0.1 $\underline{N}$ NaOH; Ca-P extracted with 0.5 $\underline{N}$ H_2SO_4; reductant soluble iron P extracted with sodium dithionite and Na-citrate; and occluded aluminum-iron P extracted with 0.1 $\underline{N}$ NaOH. Organic phosphorus was determined on separate samples by oxidation with H_2O_2. Total phosphorus was determined by the Na_2CO_3 fusion method.

The total phosphorus in the soils studied ranged between 585 and 2617 ppm of soils. It was highest in the highly calcareous Bazourye series and the lowest in the

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slightly calcareous Innsar series.

Water soluble and easily replaceable P ranged
between 0.2 to 1.6 percent of the total phosphorus. In
general, the calcareous soils contained more soluble
phosphorus than the noncalcareous soil. Amounts of Al-P
were similar in the Innsar and Zaoutar series. Al-P
in percent of the total P was the least in the highly
calcareous Bazourye series. Both Al-P and Fe-P seemed
to decrease with the increase of $CaCO_3$ content. Fe-P
occurred in a trace amount in the highly calcareous
Bazourye series. In the noncalcareous Zaoutar series it
was as high as 19 percent of the total phosphorus. This
might be due to the existence of iron and aluminum
oxides in this soil. Contrary to the belief that Ca-P
is dominant over Fe and Al-P in alkaline soils, Fe-P was
dominant in the alkaline noncalcareous Zaoutar series.
The study emphasizes that simply the alkaline reaction
cannot determine the status of phosphorus forms. It would
make a difference whether the soil is alkaline noncalcareous
or calcareous. Ca-P in the soils increased with the
$CaCO_3$ content. It was as high as 88 percent of the total
phosphorus in the highly calcareous Bazourye series. Ca-P
was only about 5 percent in the noncalcareous Zaoutar
series. Reductant soluble iron P, occluded aluminum-iron
P, and residual P decreased in the following order:
Zaoutar, Innsar, and Bazourye series. These forms seemed

to decrease with the increase of $CaCO_3$ content.
Reductant soluble iron P ranged between zero and 11 per-
cent and occluded aluminum-iron P between zero and 6 per-
cent of the total P. These forms are probably not
available to plants except through the unusual degree of
waterlogging (paddy fields) where reduction of iron
oxides may take place. Residual phosphorus ranged
between 4 to 34 percent of the total P. Organic P in the
soils increased with the organic matter content. It
ranged between 6 and 30 percent of the total P. The
Innsar series contained the highest amount of organic P.

With the effect of cropping, the fate of the
applied P over a period of one year was mainly in the
forms of Ca-P and water soluble and easily replaceable P
in the highly calcareous Bazourye series. In the slightly
calcareous Innsar series, the distribution of the applied
P was mainly in the following forms which decreased in
order: Ca-P, Al-P, organic P, and soluble P. In the non-
calcareous Zaoutar series the applied P was transformed
into a variety of forms which decreased in the following
order: residual P, Fe-P, Al-P, Ca-P, and organic P.

It can be summarized that of the active forms of
Ca-P, Al-P, and Fe-P, Ca-P was dominant in the calcareous
soils while Fe-P dominated in the noncalcareous soil.

In general, phosphorus retention in the soils, the
clays, and the sand plus silt fractions increased with

time of contact and concentration of P added. However, phosphorus retained in percent of P added decreased with concentration.

In the soils, phosphorus retention decreased with the increase of $CaCO_3$ and Ca-P contents. It increased with the quantity of Fe-P in the soils. Phosphorus retention was the highest in the noncalcareous Zaoutar series and the lowest in the highly calcareous Bazourye series. With the concentration of 400 ppm P, the P retained in 10 days was about 94 percent in the Zaoutar, 73 percent in the Innsar, and 70 percent in the Bazourye series.

To investigate the influence of iron and aluminum oxides in the clays, one sample was treated for the removal of iron and aluminum oxides while another sample was left untreated. However, from both samples $CaCO_3$ and organic matter were removed. Phosphorus retention in the Innsar and the Bazourye series was higher in the clays treated to remove the iron and aluminum oxides than the untreated clays. The explanation was that the removal of iron and aluminum oxides dispersed the clays thus increasing the surface area for more retention of phosphorus. In the noncalcareous Zaoutar series phosphorus retention was higher in the clays not treated for the iron and aluminum oxide removal than the treated clays. This might be due to the presence of a comparatively high amount

of iron and aluminum in this soil.

To investigate the influence of iron and aluminum oxides, the sand plus silt fractions were treated the same way as for the clays. In the Innsar series, the phosphorus retention in both partially clean and clean sand plus silt fractions was similar. In the Zaoutar series the partially clean fractions retained more phosphorus than the clean fractions. In the Bazourye series phosphorus retention was higher in the clean than the partially clean fractions. Although the phosphorus retention was less in the sand plus silt fractions than that of the clays, it was of considerable magnitude and merits further investigation.

Studies on the mineralogy should be done in order to understand and explain more clearly the phosphorus retaining characteristics of the sand, silt and clay fractions of the soils of Lebanon.

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APPENDIX

Table 9. Yield of wheat grain plus straw, grams, in the pots receiving low[1] and high[2] levels of P. (Tell Amara data).

Soil series	Pot receiving the low level of P	Pot receiving the high level of P
	Grain + Straw	Grain + Straw
Innsar	11.96	17.28
Zaoutar	9.57	12.81
Bazourye	16.90	21.46

[1] Pot receiving 25 mg P per 2 kg soil.

[2] Pot receiving 400 mg P per 2 kg soil.

Table 10. A-values, ppm of P applied as $NH_4(H_2PO_4)$, of the soils studied at different levels of P^{32} (Tell Amara data).

Soil series	1st level	2nd level	Average
Innsar	137	249	193
Zaoutar	171	328	249
Bazourye	138	350	244

1st level = 150 mg P^{32} per 2 kg soil.

2nd level = 450 mg P^{32} per 2 kg soil.